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VERIFICATION OF ENGLISH TRANSLATION

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I, the below named translator, hereby declare that:

My name and post office address are as stated below;

That I am knowledgeable in the English language and in the Japanese language and that I believe that the attached English translation is an accurate translation of Japanese Patent Application No. 2004-092305 filed on March 26, 2004.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Item:	Claims	1 copy
Item:	Specification	1 copy
Item:	Abstract	1 copy

Document Name: Claims

1. A high strength polyethylene multifilament having a stress Raman shift factor of not smaller than $-5.0 \text{ cm}^{-1}/(\text{cN/dTex})$.

2. The high strength polyethylene multifilament according to claim 1, wherein said multifilament has an average strength of not lower than 20 cN/dTex.

3. The high strength polyethylene multifilament according to claim 1, wherein a knot strength retention of filaments constituting the high strength polyethylene multifilament is not lower than 40%.

4. The high strength polyethylene multifilament according to claim 1, wherein CV which indicates a variation in the strengths of the filaments constituting the high strength polyethylene multifilament is not higher than 25%.

5. The high strength polyethylene multifilament according to claim 1, wherein said multifilament has an elongation at break of not lower than 2.5%.

6. The high strength polyethylene multifilament according to claim 1, wherein each of monofilaments has a fineness of not higher than 10 dTex.

7. The high strength polyethylene multifilament according to claim 1, wherein the melting point of the filaments is not lower than 145°C.

Document Name: Specification

Title of the Invention: High Strength Polyethylene Fiber

Technical Field

[0001]

The present invention relates to novel high strength polyethylene multifilaments applicable to a wide range of industrial fields such as high performance textiles for sportswears and safety outfits (e.g., bulletproof/protective clothing, protective grooves, etc.), rope products (e.g., tugboat ropes, mooring ropes, yacht ropes, ropes for constructions, etc.), braided products (e.g., fishing lines, blind cables, etc.), net products (e.g., fisheries nets, ball-protective nets, etc.), reinforcing materials or non-woven cloths for chemical filters, butterfly separators, etc., canvas for tents, etc., and reinforcing fibers for composites which are used in sports goods (e.g., helmets, skis, etc.), speaker cones, prepregs and reinforcement of concrete.

Background of the Invention

[0002]

High strength polyethylene multifilaments obtained by so-called "gel spinning method" using ultra-high molecular weight polyethylenes as raw materials are known to have such high strength and high elastic modulus that any of the prior art has never achieved, and such high strength polyethylene multifilaments have already been widely used in various industrial fields (cf. Patent Literature 1 and Patent Literature 2).

[0003]

Patent Literature 1: JP-B-60-47922 (1985)

[0004]

Patent Literature 2: JP-B-64-8732 (1989)

[0005]

High strength polyethylene multifilaments recently have come into wide use in not only the above-described fields but also other fields, and are earnestly demanded to have more uniform and higher strength and higher elastic modulus relative to required performance.

Disclosure of the Invention

Problem to be Solved by the Invention

[0006]

One of effective means to satisfy the above wide range of demands is to decrease the interior defects of multifilaments as much as possible, and further, filaments constituting the multifilament are required to be uniform. The conventional gel spinning method has been hard to suppress the internal defective structures of filaments to sufficiently low levels, and the filaments constituting such a multifilament have large variation in the strengths thereof. The present inventors have inferred the causes for these disadvantages as follows.

[0007]

A super drawing operation becomes possible by employing the conventional gel spinning method, so that the resultant multifilament can have high strength and high elastic modulus, with the result that the filaments are so highly crystallized and ordered in their structures that the long periodic structures thereof can not be observed in the measurement of small-angle X-ray scattering. On the other hand, defective structures (non-uniform structures) which can not be eliminated anyhow are formed in the filaments, as will be described later. The agglomeration

of such defective structures induces a wide stress distribution inside the filaments when a stress is applied to the filaments. The skin-core structures of the filaments are considered as one of these defective structures.

[0008]

A stress distribution which occurs in the structure of a filament can be measured, for example, by the Raman scattering method as indicated by Young et al (Journal of Materials Science, 29, 510 (1994)). The Raman band, that is, a normal vibration position, is determined by solving an equation which consists of the constant of the force of the molecular chains composing the filament, and the configuration of the molecule (the internal coordinates) (Molecular Vibrations by E.B. Wilson, J.C. Decius and P.C. Cross, Dover Publications (1980)). For example, this phenomenon has been theoretically described by Wools et al as follows: the molecules of the filament distort together with the distortion of the filament, so that, consequently, the normal vibration position changes (Macromolecules, 16, 1907 (1983)). When a structural non-uniformity such as agglomeration of defects is present in the filament, stresses induced upon distorting the filament from an external are different depending on the sites of the filament.

This change can be detected as a change in the band profile. Therefore, the investigation of a relationship between the strength of the filament and a change in the Raman band profile, found when a stress is applied to the filament, makes it possible to quantitatively determine a stress distribution induced in the filament.

In other words, as will be described later, a filament small in structural non-uniformity tends to take a value within a region including a Raman shift factor.

A high strength polyethylene filament obtained by the disclosed "gel spinning method" has a very high tensile strength because of its highly oriented structure, but is easily broken by a relatively low stress, as well as the knot strength thereof, when the filament is bent. When the filament further has a non-uniform structure in its sectional direction, like a skin-core structure, the filament is more easily broken, if it is in a bent state.

As a result of the inventors' intensive studies, it is found that a filament small in structural non-uniformity is strong against pulling while it is being bent. In other words, in a filament small in structural non-uniformity, the ratio of the knot strength to the tensile strength becomes higher.

[0009]

Therefore, one of the defects of the high strength polyethylene multifilaments obtained by the disclosed "gel spinning method" is that monofilaments spun from nozzle holes have variable strengths depending on their conditions after the spinning, in comparison with filaments obtained by the usual melt-spinning method or the like. Therefore, there is a problem in that a yarn consisting of such filaments includes some filaments whose strengths are markedly low, as compared with the average fineness of the filaments of the yarn. When the yarn includes such filaments having strengths lower than the average strength, the following disadvantage is caused. For example, when such yarns are used for a fishing line, a rope, a

bulletproof/protective clothing or the like, and when such yarns are subject to abrasion, and if such yarns are made of filaments having variable thickness, stresses tend to concentrate on a thinner portion of such a product, so that this product ruptures. Also in the manufacturing steps for such a product, troubles due to the cutting of the filaments are likely to occur, which gives an adverse influence on the productivity.

The present invention is therefore intended to provide a high strength polyethylene multifilament which is excellent in uniformity and has a narrow variation in the strengths of monofilaments, by improving the foregoing problems. The variation in monofilament strength can be clearly defined by a CV value (described later).

[0010]

The present inventors have intensively studied and succeeded in the development of a novel high strength polyethylene multifilament with an uniform internal structure, having a narrow variation in the strengths of its filaments. The conventional gel spinning methods have been hard to provide these characteristics. Thus, the present invention is accomplished as the result of the above development.

Means for Solving the Problem

[0011]

The present invention provides the following.

1. A high strength polyethylene multifilament having a stress Raman shift factor of not smaller than $-5.0 \text{ cm}^{-1}/(\text{cN/dTex})$.
2. The high strength polyethylene multifilament defined in the above item 1, wherein the multifilament has

an average strength of not lower than 20 cN/dTex.

3. The high strength polyethylene multifilament defined in the above item 1, wherein a knot strength retention of filaments constituting the high strength polyethylene multifilament is not lower than 40%.

4. The high strength polyethylene multifilament defined in the above item 1, wherein CV which indicates a variation in the strengths of the monofilaments constituting the high strength polyethylene multifilament is not higher than 25%.

5. The high strength polyethylene multifilament defined in the above item 1, wherein the multifilament has an elongation at break of not lower than 2.5%.

6. The high strength polyethylene multifilament defined in the above item 1, wherein each of the monofilaments has a fineness of not higher than 10 dTex.

7. The high strength polyethylene multifilament defined in the above item 1, wherein the melting point of the filaments is not lower than 145°C.

Effect of the Invention

[0012]

The present invention makes it possible to provide an uniform and high strength polyethylene multifilament which has as a few internal defects as possible that the conventional gel spinning method has never achieved to such a sufficiently low level, and which has a small variation in the strengths of the filaments constituting the multifilament.

Best Modes for Carrying out the Invention

[0013]

Hereinafter, the present invention will be described

in detail.

One of the most distinguishing features of the high strength polyethylene multifilament according to the present invention is that the stress Raman shift factor is not smaller than $-5.0 \text{ cm}^{-1}/(\text{cN/dTex})$. As described above, this stress Raman shift factor is to quantitatively indicate a stress distribution induced in the filament and thus is very effective as an index for indicating uniformity of the filament internal structure. To manufacture a polyethylene multifilament whose stress Raman Shift factor is not smaller than $-5.0 \text{ cm}^{-1}/(\text{cN/dTex})$ as in the invention of the present application, manufacturing methods described later are exemplified. The stress Raman shift factor is preferably from -4.0 to $-5.0 \text{ cm}^{-1}/(\text{cN/dTex})$, more preferably from -3.0 to $-4.0 \text{ cm}^{-1}/(\text{cN/dTex})$. When the stress Raman shift factor is smaller than $-5.0 \text{ cm}^{-1}/(\text{cN/dTex})$, undesirably, there may induced a decrease in the strength of the filament because of a possible structural defect in the filament, so that the object of the present invention can not be achieved.

[0014]

The average strength of the high strength polyethylene multifilament of the present invention is not smaller than 20 cN/dTex , preferably not smaller than 30 cN/dTex , more preferably not smaller than 35 cN/dTex , still more preferably not smaller than 40 cN/dTex , far still more preferably not smaller than 45 cN/dTex . While the upper limit thereof is not particularly limited, it is not larger than 60 cN/dTex .

[0015]

The retention of the knot strength of the

monofilaments constituting the high strength polyethylene multifilament of the present invention is preferably not lower than 40%. This condition indicates that the polyethylene multifilament of the present invention still can have a high tensile strength even in a bent state, and this property suggests very high advantages of the polyethylene multifilament of the present invention for use in a variety of ropes, fishing lines, a variety of braids, nets such as fisheries nets, etc. Such a polyethylene multifilament can be manufactured by a method as will be described later, wherein it is especially effective to increase a difference in speed between a gel-like filament discharged from a spinneret and a cooling medium. The retention of the knot strength of the monofilament is preferably not lower than 45%, more preferably not lower than 50%. While the upper limit thereof is not limited, it is appropriately not higher than 80%.

[0016]

The CV which indicates a variation in the strengths of the monofilaments constituting the high strength polyethylene multifilament of the present invention is preferably not higher than 25%. This condition makes it possible to solve one of the conventional problems of ultrahigh molecular polyethylene filaments, i.e., variation among each of the monofilaments. Such a problem can be solved by employing a manufacturing method as will be described later. When the CV is higher than 25%, stresses tend to concentrate on a filament having a lower strength, which is likely to decrease an average strength. The CV is preferably not higher than 23%, more preferably not higher than 22%, still more preferably not higher than 20%.

[0017]

The elongation at break in the high strength polyethylene multifilament of the present invention is preferably not lower than 2.5%. When the elongation at break is lower than 2.5%, control of the tension of filaments while are being evenly pulled and arrayed becomes difficult. The elongation at break is more preferably not lower than 3.0%.

[0018]

The fineness of the monofilaments of the high strength polyethylene multifilament of the present invention is preferably not larger than 10 dTex, more preferably from 0.1 to 5.0 dTex. The melting point of the monofilaments is preferably not lower than 145°C.

[0019]

Next, a method for manufacturing the high strength polyethylene multifilament of the present invention will be described. It is needed that a high molecular weight polyethylene, as a raw material for the multifilament of the present invention, should have a limiting viscosity $[\eta]$ of not smaller than 5, preferably not smaller than 8, still more preferably not smaller than 10. When the limiting viscosity is smaller than 5, the resultant high strength filament can not have a desired strength exceeding 20 cN/dtex. While the upper limit thereof is not limited, it is desirably not larger than 30, in consideration of operability such as spinning, etc.

[0020]

An ultra-high molecular weight polyethylene to be used in the present invention has repeating units of substantial ethylene. The ultra-high molecular weight polyethylene may

be a copolymer of ethylene with a small amount of other monomer such as α -olefin, acrylic acid or its derivative, methacrylic acid or its derivative, vinylsilane or its derivative, or the like; or the ultra-high molecular weight polyethylene may be a blend of some of these copolymers, a blend of such a copolymer with an ethylene homopolymer or a blend of such a copolymer with a homopolymer of other α -olefin or the like. Particularly, the use of a copolymer of ethylene with α -olefin such as propylene, butene-1 or the like is preferable, since short or long chain branches are contained in a spinning solution to a certain degree by using such a copolymer, which is desirable for the manufacturing of the multifilament of the present invention, particularly for stable spinning and drawing.

However, a too large content of a component other than ethylene makes it hard to draw filaments. Therefore, the content of other component is not larger than 0.2 mol %, preferably not larger than 0.1 mol % in monomer unit, so as to obtain a filament having a high strength and high elastic modulus. Of course, the ultrahigh molecular weight polyethylene may be a homopolymer of an ethylene monomer alone.

[0021]

As a method of the present invention, preferably, such a high molecular weight polyethylene is dissolved in a volatile organic solvent such as decalin, tetralin or the like. The use of a solvent which is solid or non-volatile at a room temperature is undesirable since the spinning efficiency becomes very poor. This is described below. When a volatile solvent is used, the volatile solvent present on the surface of a gel-like filament discharged

from a spinneret slightly evaporates in the early stage of the spinning step. Although not definitely confirmed, the cooling effect attributed to the latent heat in association with the evaporation of the solvent is considered to stabilize the yarn-making condition.

The concentration of the ultra-high molecular weight polyethylene is preferably not higher than 30 wt.%, more preferably not higher than 20 wt.%. It is necessary that an optimal concentration should be selected according to the limiting viscosity $[\eta]$ of the ultra-high molecular weight polyethylene as the raw material. In the spinning step, preferably, the temperature of the spinneret is set at a temperature 30°C higher than the melting point of the polyethylene as the raw material and lower than the boiling point of the solvent. This is because the viscosity of the polymer is too high at temperatures close the melting point of the polyethylene, with the result that the resulting filaments can not be quickly pulled up. On the other hand, when the temperature of the spinneret is higher than the boiling point of the solvent, the solvent boils immediately after the discharge from the spinneret, with the result that the resulting filaments frequently break just below the spinneret.

[0022]

Next, the most important factors for the method for manufacturing uniform polyethylene multifilaments according to the present invention will be described.

One of such factors is that a previously rectified inert gas of high temperature is individually fed to each of discharged solutions from the orifices of a nozzle. The velocity of the inert gas is preferably not higher than 1

m/second. When the velocity of the inert gas is higher than 1 m/second, the evaporation rate of the solvent becomes higher, so that a non-uniform structure tends to form along the sectional direction of the resulting filament, and what is worse, the filament may break. The velocity of the inert gas is preferably from 0.01 to 0.5 m/second.

The temperature of the inert gas is preferably within a range of $\pm 10^{\circ}\text{C}$ of the nozzle temperature, more preferably $\pm 5^{\circ}\text{C}$ thereof. The individual feeding of the inert gas to each of the discharged filament-like solutions makes it possible to uniform the cooling conditions for the respective filament-like solutions, so that non-drawn filaments having uniform structures can be obtained. Desired uniform and high strength polyethylene filaments are supposed to be obtained by evenly drawing the above non-drawn filaments having the uniform structures.

[0023]

Another factor is that the discharged gel-like filaments from the spinneret are rapidly and uniformly cooled, while careful attentions being paid to a difference in speed between the cooling medium and the gel-like filaments.

The cooling speed is preferably not lower than $1,000^{\circ}\text{C}/\text{second}$, more preferably from 3,000 to $1,500^{\circ}\text{C}/\text{second}$.

As for the speed difference, the integrated value of speed differences, i.e., the accumulated speed difference is preferably not larger than 30 m/minute, more preferably from 0 to 15 m/minute.

Under the foregoing conditions, non-drawn filaments

excellent in uniformity can be obtained. In this regard, the accumulated speed difference is calculated by the following equation:

$$\text{Accumulated speed difference} = \int (\text{the speed of the filament-like solution} - \text{the speed of the cooling medium in the filament-pulling direction}).$$

The gel-like filaments are rapidly and uniformly cooled to thereby obtain non-drawn filaments having uniform structures in the sectional directions.

When the cooling speed for the discharged gel-like filaments is lower, the internal structures of the resulting non-drawn filaments become non-uniform. Herein, description is made on a multifilament as an example. When the cooling conditions to the respective filaments constituting a multifilament are different, non-uniformity among each of the filaments is accelerated. When the speed difference between the pulled filaments and the cooling medium is large, a frictional force acts between the pulled filaments and the cooling medium, which makes it hard to pull the filaments at a sufficient spinning speed.

To obtain an appropriate cooling speed, it is recommended to use a liquid having a large coefficient of heat-transfer as the cooling medium. Above all, the use of a liquid incompatible with a solvent to be used is preferable. For example, water is preferably used for its availability.

[0024]

To reduce the accumulated speed difference, the following method is considered to be effective, although this method does not limit the scope of the present

invention in any way. For example, a funnel is attached at the center of a cylindrical bath so as to allow a liquid and gel-like filaments to simultaneously flow, to thereby pull up them together; or the gel-like filaments are allowed to flow along a liquid which drops like waterfall, to thereby simultaneously pull them together. By employing any of these methods, the accumulated speed difference can be reduced, in comparison with that found when gel-like filaments are cooled using a stationary liquid.

[0025]

The resulting non-drawn filaments are heated and drawn at a certain draw ratio, while removing the solvent. As the case may be, the non-drawn filaments are drawn in multistage so as to obtain high strength polyethylene filaments having highly uniform internal structures as described above. In this regard, the deforming speed of the filament while being drawn is taken as an important parameter. When the deforming speed of the filaments is too high, undesirably, the filaments break before a sufficient draw ratio can be obtained. When this deforming speed is too low, the molecular chains in the filaments relax while the filaments are being drawn. As a result, the filaments become thinner by the drawing, however, have poor physical properties. The deforming speed of the filaments is preferably from 0.005 to 0.5 s^{-1} , more preferably 0.01 s^{-1} or more and 0.1 s^{-1} or less. The deforming speed of the filaments can be calculated from the draw ratio, the drawing speed and the length of the heating section of an oven.

That is, the deforming speed can be determined by the equation:

Deforming speed (s^{-1}) = $(1 - 1/\text{the draw ratio}) \times$
the drawing speed/the length
of the heating section

To obtain a filament having a desired strength, the draw ratio of the filaments is not smaller than 10, preferably not smaller than 12, still more preferably not smaller than 15.

[0026]

Hereinafter, the methods and conditions for measuring the characteristics of the multifilament of the present invention will be described.

[0027]

(Strength, Elongation Percentage and Elastic Modulus of Multifilament)

The strength and elastic modulus of the multifilament of the present invention were measured as follows, using "Tensilon" (ORIENTECH): a sample with a length of 200 mm (i.e., the length between chucks) of the multifilament was extended at an elongation rate of 100%/minute under an atmosphere of 20°C and a relative humidity of 65% so as to measure a deformation-stress curve. The strength (cN/dTex) and the elongation percentage (%) were calculated from a stress and an elongation at the breaking point, and the elastic modulus (cN/dTex) was calculated from a tangent which formed the highest slope at and around the origin of the curve. Each of the values was an average of the found values obtained from 10 measurements.

[0028]

(Strength of Monofilament)

The strength and elastic modulus of a filament (or monofilament) were measured using samples which are 30

monofilaments arbitrarily selected from one multifilament to be measured. Each one monofilament constituting the multifilament was sampled. In case of a multifilament comprising less than 30 monofilaments, all the monofilaments were used as objects to be measured.

Out of each monofilament with a length of about 2 m, one meter thereof was cut and weighed, and the weight was converted in terms of 10,000 m to measure the fineness (dTex). In this regard, when the length of this monofilament (1 m) was measured, a sample with a constant length was made by applying a load which was about one tenth of the monofilament. The rest of this monofilament was used to measure the strength thereof by the same method as above. The CV was calculated by the following equation:

$$CV = \frac{\text{a standard deviation of the strength of a monofilament}}{\text{an average of the strengths of monofilaments}} \times 100$$

[0029]

(Knot Strength Retention of Monofilament)

The strength and elastic modulus of a filament (or monofilament) were measured using samples which were 30 monofilaments arbitrarily selected from one multifilament to be measured. Each one monofilament constituting the multifilament was sampled. In case of a multifilament comprising less than 30 monofilaments, all the monofilaments were used as objects to be measured.

Out of each monofilament with a length of about 2 m, one meter thereof was cut and weighed, and the weight was converted in terms of 10,000 m to measure the fineness (dTex). In this regard, when the length of this monofilament (1 m) was measured, a sample with a constant

length was made by applying a load which was about one tenth of the monofilament. The rest of this monofilament was knotted at its center to make a knot, and was then subjected to a tensile test in the same method as in the measurement of the strength of the filament. In this regard, the knot was made according to the method shown in Fig. 3 described in JIS L1013, and the direction of knotting was always the same as the direction **b** shown in Fig. 3.

Knot strength retention = an average of the knot
strengths of the monofilaments/an average of
the strengths of the monofilaments X 100

[0030]

(Limiting Viscosity)

The specific viscosities of variously diluted solutions were measured in decalin of 135°C with a Ubbelohde type capillary viscometer, and the specific viscosities were plotted relative to the concentrations of the solutions. Then, the limiting viscosity was determined from an extrapolation point to the origin of a linear line obtained by the approximation of the least squares of the plots. In this measurement, a sample was divided or cut into pieces with lengths of about 5 mm, and the cut pieces were admixed with 1 wt.% of an antioxidant ("Yoshinox" manufactured by Yoshitomi Seiyaku) based on the weight of the polymer, and the mixture was dissolved while being stirred, at 135°C for 4 hours, to thereby prepare a measuring solution.

[0031]

(Measurement with Differential Scanning Calorimeter)

A differential scanning calorimeter DSC 7 manufactured

by PerkinElmer was used. A sample was cut into pieces with lengths of 5 mm or less, and the cut pieces (about 5 mg) were enveloped in an aluminum pan, and the aluminum pan including the sample pieces was heated from a room temperature to 200°C at an elevation rate of 10°C/minute, referring to an empty aluminum pan of the same type, to determine an endothermic curve. The temperature of the top of the melting peaks which appeared on the lowest temperature side of the endothermic curve was defined as a melting point.

[0032]

(Measurement of Raman Scattering Spectrum)

The Raman scattering spectrum was measured as follows. As a Raman spectrometer, System 1000 manufactured by Renishaw was used. As a light source, helium neon laser (wavelength: 633 nm) was used, and a yarn was placed with its axis in parallel to a polarized light direction for measurement. The yarn was slit into monofilaments, and one of the monofilaments was stuck on a paper board having a rectangular opening (50 mm (vertical) X 10 mm (lateral)) so that the center longer axis of the opening could be aligned with the axis of the filament, and both ends of the filament were adhered with an epoxy adhesive (Araldite) and was then left to stand for 2 or more days. After that, the filament on the paper board was attached to a jig controllable in length with a micrometer, and the paper board having the filament thereon was carefully cut off. Then, a predetermined load was applied to the filament, and the filament under the load was placed on the stage of the microscope of the Raman scattering apparatus so as to measure the Raman spectrum thereof. In this measurement, a

stress acting on the filament and the distortion of the filament were simultaneously measured. In the Raman measurement, data of the filament were collected in the Static Mode, provided that the resolution per one pixel was set at not larger than 1 cm^{-1} within a measuring range of 850 cm^{-1} to $1,350\text{ cm}^{-1}$. A peak used for the analysis was taken from a band of $1,128\text{ cm}^{-1}$ attributed to the symmetric stretching mode of a C-C backbone bond. To correctly determine the center of gravity of the band and the width of the line (the standard deviation of a profile having its center on the center of gravity of the band, and a square root of secondary moment), the profile was approximated as a synthesis of two Gaussian functions, so that the curves could be successfully fitted to each other. It was found that, when the filament was distorted, the peaks of the two Gaussian functions did not coincide with each other, and that the distance between each of the peaks became longer. According to the present invention, the position of the peak of the band was not taken as a top of the peak profile, and the center of gravity of two Gaussian peaks was defined as the position of the peak of the band. This definition was represented by the equation 1 (a position of the center of gravity, $\langle x \rangle$). A graph was made by plotting the positions of center of gravity of the band $\langle x \rangle$ and the stress applied to the filament. The slope of the approximated curve passing through the origin which was obtained by the method of least squares of the resultant plots was defined as a stress Raman shift factor. The same measurements were conducted on three filaments (monofilament) arbitrarily removed, and an average of the found values was defined as a central value of a

multifilament.

[0033]

$$\langle x \rangle = \int x f(x) dx / \int f(x) dx$$

$$f(x) = f_1(x - a) + f_2(x - b)$$

wherein f_i represents a Gaussian function.

[0034]

(Examples 1 to 3)

A slurry-like liquid mixture was prepared by mixing a ultra-high molecular weight polyethylene having a limiting viscosity of 21.0 dl/g, and decahydronaphthalene in the weight ratio 8 : 92. This mixture was dissolved with a twin-screwed extruder equipped with a mixer and a conveyer, to obtain a transparent and homogenous solution. This solution was discharged at a rate of 1.8 g/minute from an orifice with a diameter of 0.8 mm, having 30 holes circularly disposed, maintained at 178°C. The discharged solutions were allowed to pass through a cylindrical tube filled with water steadily flowing, via an air gap with a length of 10 mm, so as to evenly cool them. The resultant gel-like filaments were pulled at a rate of 60 m/minute, without the removal of the solvent. In this connection, the cooling rate of the gel-like filaments was 9,669°C/second, and the accumulated speed difference was 5 m/minute. Then, the gel-like filaments were drawn at a draw ratio of 3 in a heated oven under a nitrogen atmosphere, without winding them up. Then, the drawn filaments were wound up. Next, the filaments were drawn at 149°C and at a draw ratio which was variously changed up to maximum 6.5. The physical properties of the resultant polyethylene filament are shown in Table 1.

[0035]

(Examples 4 and 5)

A slurry-like mixture of a ultra-high molecular weight polyethylene polymer having a limiting viscosity of 19.6 dl/g (10 wt.%) and decahydronaphthalene (90 wt.%) was dispersed and dissolved with a screw type kneader set at 230°C, and the resultant solution was fed to a spinneret with a diameter of 0.6 mm, which had 400 holes and was set at 177°C, at a discharge rate of 1.2 g/min./hole, using a light pump. Polyethylene filaments were obtained in the same manners as in Example 1, except that a nitrogen gas was evenly applied to the respective discharged filament-like solutions at a rate of 0.1 m/second, using collar-like quench devices independently provided just below the respective nozzles, while paying careful attentions to the rectificated flow of the nitrogen gas, so that a minute amount of decalin was evaporated from the surfaces of the resulting filaments, and that the filaments were allowed to pass through an air gap under a nitrogen atmosphere. In this regard, the draw ratio in the second step was 4.5 or 6.0. The temperature of the nitrogen gas used for quenching was controlled at 178°C. The air gap was not controlled in temperature. The values of the physical properties of the resultant filaments are shown in Table 1. The filaments were found to be very excellent in uniformity and to have high strength.

[0036]

(Comparative Example 1)

A slurry-like mixture of a ultra-high molecular weight polyethylene having a limiting viscosity of 19.6 dl/g (10 wt.%) and decahydronaphthalene (90 wt.%) was dispersed and dissolved with a screw type kneader set at 230°C, and the

resultant solution was fed to a spinneret with a diameter of 0.6 mm, which had 400 holes and was set at 175°C, at a discharge rate of 1.6 g/min./hole, using a light pump. A nitrogen gas controlled at 178°C was applied at a rate of 0.1 m/second to the discharged filament-like solutions as evenly as possible, using collar-like quench devices independently provided just below the respective nozzles, while paying careful attentions to the rectificated flow of the nitrogen gas, so as to evaporate a minute amount of decalin from the surfaces of the resultant filaments. The residual decalin on the surfaces of the filaments was further evaporated by a nitrogen flow controlled at 115°C, and the resultant filaments were pulled up at a rate of 80 m/minute with a Nelson-like roller arranged on the downstream side from the nozzles. In this regard, the length of the quench section was 1.0 m; the cooling rate of the filaments was 80°C/second; and the accumulated speed difference was 80 m/minute. Subsequently, the resultant filaments were drawn at a draw rate of 4.0 in an oven heated at 125°C, and were sequentially drawn at a draw ratio of 4.1 in an oven heated at 149°C. Uniform filaments could be obtained without breaking. The physical properties of the filaments are shown in Table 1.

[0037]

(Comparative Example 2)

Drawn filaments were obtained in the same manners as in Example, except that a nitrogen gas flow controlled at 50°C was applied to the discharged filament-like solutions at a rate of 1.2 m/second as evenly as possible, from a position 10 mm just below the orifice, while paying careful

attentions to the rectificated flow of the nitrogen gas, to thereby obtain gel-like filaments. The cooling rate of the filaments was 167°C/second, and the accumulated speed difference was 8 m/minute.

[0038]

(Comparative Example 3)

A slurry-like mixture of a polymer (C) (15 wt.%) as a main component of a ultra-high molecular weight polymer having a limiting viscosity of 10.6 and paraffin wax (85 wt.%) was dispersed and melted with a screw type kneader set at 230°C, and the resulting solution was fed to spinneret with a diameter of 1.0 mm, which had 400 holes and was set at 190°C, at a discharge rate of 2.0 g/minute/hole, using a light pump. The resultant filament-like solutions were allowed to pass through an air gap with a length of 30 mm, and were then immersed in a spinning bath filled with n-hexane at 15°C. After the immersion, the filaments were pulled up with a Nelson-like roller at a rate of 50 m/minute. The cooling rate of the filaments was 4,861°C/second, and the accumulated speed difference was 50 m/minute. Sequentially, the filaments were drawn at a draw ratio of 3.0 in an oven heated at 125°C, and were further drawn at a draw ratio of 3 in an oven heated at 149°C, and were then once more drawn at a draw ratio of 1.5. Uniform textile could be obtained without breaking. The physical properties of the filaments are shown in Table 1.

[0039]

[Table 1] (Part 1)

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Total draw ratio	16.0	17.5	19.5	13.5	18.0
Fineness (dTex)	45	41	37	591	440
Fineness of monofilament (dTex)	1.5	1.4	1.2	1.5	1.1
Strength (CN/dTex)	38	42	49	43	47
Elongation at break (%)	4.2	4.1	4.0	4.2	4.2
Stress Raman shift factor	-3.5	-3.4	-3.3	-3.4	-3.3
Knot strength retention of monofilament (%)	47	50	54	46	54
Variation in strengths of monofilaments (CV %)	20	22	23	15	16
Melting point (°C)	146.2	146.6	146.6	146.2	146.3

[Table 1] (Part 2)

	C. Ex. 1	C. Ex. 2	C. Ex. 3
Total draw ratio	16.4	16.4	13.5
Fineness (dTex)	490	490	1,780
Fineness of monofilament (dTex)	1.2	1.2	4.4
Strength (CN/dTex)	29.2	30.1	28
Elongation at break (%)	3.4	3.4	3.3
Stress Raman shift factor	-5.3	-5.1	-5.5
Knot strength retention of monofilament (%)	43	44	38
Variation in strengths of monofilaments (CV %)	22	20	40
Melting point (°C)	145.6	146.0	148.0

INDUSTRIAL APPLICABILITY

[0040]

The high strength polyethylene filaments according to the present invention has a high strength, a high elastic modulus and a uniform internal structure. Therefore, such a high strength polyethylene filament is applicable in a wide range of industrial fields such as high performance textiles for sportswears, safety outfits (e.g., bulletproof/protective clothing, protective grooves, etc.) and the like, rope products (e.g., tugboat ropes, mooring ropes, yacht ropes, ropes for construction, etc.), braided ropes (e.g., fishing lines, blind cables, etc.), net products (e.g., fisheries nets, ball-protective nets, etc.), reinforcing materials or non-woven cloths for chemical filters, battery separators, etc., canvas for tents, etc., and reinforcing fibers for composites which are used in sports goods (e.g., helmets, skis, etc.), speaker cones, prepregs, concrete, etc.

Document Name: Abstract

Purpose: To provide a novel polyethylene textile having a high strength and a uniform internal structure, and showing a narrow variation in the strengths of monofilaments constituting the textile, which has been difficult to be provided by the conventional gel spinning method.

Solution: A high strength polyethylene multifilament having a stress Raman shift factor of not smaller than $-5.0 \text{ cm}^{-1}/(\text{cN/dTex})$ and an average strength of not lower than 20 cN/dTex, wherein a knot strength retention of monofilaments constituting the multifilament is not lower than 40%; CV which indicates a variation in the strengths of the monofilaments constituting the multifilament is not higher than 25%; said multifilament has an elongation at break of 2.5% or more and 6.0% or less; each of the monofilaments has a fineness of not higher than 10 dTex; and the melting point of the filaments is not lower than 145°C.